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Carbon-Based Electrodes for Sensitive Electroanalytical Determination of Aminonaphthalenes

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Abstract: The electroanalytical performance of bare glassy carbon electrodes (GCE) for the determination of 1-aminonaphthalene (1-AN) and 2-aminonaphthalene (2-AN) was compared with GCE modified by a Nafion permselective membrane or multiwalled carbon nanotubes and with other types of carbon-based materials, carbon film and boron doped diamond. Nafion-modified GCE gave the highest sensitivity and lowest detection limit (0.4 μmol L^{-1}) for differential pulse voltammetric determination of 1-AN. Electrochemical impedance spectroscopy gave information about the processes at the electrode surface. Simultaneous determination of 1-AN and 2-AN in a mixture at GCE and their determination in model samples of river water is presented.

Keywords: Aminonaphthalenes · Carbon electrode materials · Nafion · Multiwalled carbon nanotubes · Differential pulse voltammetry · Electrochemical impedance spectroscopy

1 Introduction

Aminonaphthalenes are aminoderivatives of polycyclic aromatic hydrocarbons (APAHs), significant pollutants of working and living environments, and with carcinogenic, mutagenic, and teratogenic effects. 2-aminonaphthalene (2-AN) is a proven human carcinogen [1], and for 1-aminonaphthalene (1-AN) mutagenic effects have been verified [2]. The first reports on the analytical determination of 2-AN were in the 1960s [3]. Historically, water, urine, and textile samples have been analysed for 2-AN content by gas chromatography (GC) and liquid chromatography-mass spectrometry (LC-MS). These methods permit detection at concentrations down to the pmol L^{-1} level. Recent studies involve the use of GC-MS to determine the concentrations of 2-AN (in derivative form) in cigarette smoke and in the urine of smokers. This method, together with HPLC-MS, is the most often used for various matrices (reviewed in [1]). Modern electrochemical methods represent an independent option to these more expensive chromatographic-MS hyphenated methods. Because amino groups on the aromatic skeleton can easily undergo electrochemical oxidation, voltammetry is an appropriate tool for the monitoring of APAHs in various environmental and biological matrices. Some recently used electrochemical methods for 1-AN and/or 2-AN include the use of boron doped diamond electrodes (BDDE) in Britton-Robinson (BR) buffer pH 7.0 [4], where micromolar limits of detection (*LOD*) were achieved. In other studies of aromatic amines at BDDE, e.g. aminobiphenyls [5] and 3-aminofluoranthene [6], fouling of the electrode surface by passivating intermediates and end products of the electrode reaction was observed. The passivating films covering the electrode surface are created by dimerization and by further polymerization of nitrene cation radical formed in first one-electron step of oxidation of the amino group [7–9]. Further, a nanocomposite-modified glassy carbon electrode (GCE) [10] was used and both analytes were determined after their accumulation using a α-, β-, or γ-cyclodextrin modified carbon paste electrode or a β-cyclodextrin modified screen printed electrode [11]. Electrochemical detection has been also successfully used in connection with liquid flow techniques including HPLC [4,12,3], and capillary electrophoresis [4,5].

Glassy carbon is frequently used as an inexpensive sensor electrode material with excellent electrical and mechanical properties, wide potential range, extreme chemical inertness, high resistance to acid attack, impermeability to gases and relatively reproducible performance [6]. Carbon nanotubes (CNT) have been recently used for a wide range of applications, because they represent an important group of nanoscale materials with interesting properties such as high surface area per volume, high electrical conductivity, and interesting electronic properties [17–20]. Their electroactivity is attributed to the presence of reactive groups on the surface, the electrocatalytic effects being associated with structural defects [1,22]. Generally, higher peak currents, and a lower overpotential are observed at CNT modified electrodes [23–25]. Due to these characteristics, CNT have received

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enormous attention for the preparation of electrochemical sensors [20,26–28]. Nafion, a synthetic polymer, is a perfluorosulfonate membrane with high permselectivity of cations vs. anions [29]. It is often used to protect the electrode surface from organic substances present in natural samples that adsorb at the electrode surface, in this way diminishing the response to analyte [30–32].

The present work reports a comparison of bare carbon-based electrodes (glassy carbon (GCE), carbon film (CFE) and boron doped diamond (BDDE)) with GCE surface modified by Nafion permselective membrane or multiwalled carbon nanotubes (MWCNT) for the determination of 1-AN and 2-AN. Electrochemical impedance spectroscopy was employed for the investigation of the electrode interface processes. Simultaneous determination of the two compounds, 1-AN and 2-AN, as well as their determination in model river water samples, is also described.

2 Experimental

2.1 Reagents

The 1×10^{-2} mol L^{-1} stock solutions of 1-AN (Sigma-Aldrich, 98 %), and 2-AN (Sigma-Aldrich, 95 %) were prepared by dissolving each compound in deionized water (Millipore Q-plus System, Millipore, USA). More diluted solutions of 1-AN and 2-AN were prepared by appropriate dilution of stock solutions with Britton–Robinson (BR) buffer. BR buffers were prepared by mixing a solution of 0.04 mol L^{-1} phosphoric, acetic (both p.a., Riedel-de Haën, Laborchemikalien, Germany) and boric acid (May&Baker, England), with an appropriate amount of 0.2 mol L^{-1} sodium hydroxide solution (p.a., Riedel-de Haën, Laborchemikalien, Germany). For modification of electrode surfaces, 1 % (v/v) Nafion (5 % v/v, Aldrich) prepared in pure ethanol (p.a., Merck, Germany) and 1 % (m/v) MWCNT (~95 % purity, 30 ± 10 nm diameter, 1–5 μm length, NanoLab, USA) dispersed in *N,N*-dimethylformamide (DMF, analytical grade, Fluka, Switzerland) were used.

2.2 Apparatus

Voltammetric measurements were carried out using a computer controlled IviumStat electrochemical analyser with IviumSoft software (version 2.024, Ivium Technologies, The Netherlands). In differential pulse voltammetry (DPV), a pulse amplitude of 50 mV, pulse width 50 ms, potential step 2 mV and scan rate 5 mV s^{-1} were used, unless otherwise indicated.

All electrochemical measurements were performed in a three-electrode arrangement, using a silver chloride reference electrode (Ag|AgCl, 3 mol L^{-1} KCl) and a platinum wire auxiliary electrode. The following electrodes were used as working electrodes: 1) a laboratory-made disc GCE with active geometric area of 23.7 mm^2; 2) a carbon film electrode (CFE) with active geometric area of 20.0 mm^2 (the preparation and characterization of this electrode has been presented elsewhere [33,34]); 3) a laboratory-made boron-doped diamond electrode (BDDE) with active geometric area of 12.6 mm^2 [35] made from a microcrystalline boron-doped diamond film deposited on silica wafers, the BDD film having been prepared and characterized by procedures described previously [36].

Electrochemical impedance spectroscopy (EIS) measurements were performed using a Solartron 1250 Frequency Response Analyser, coupled to a Solartron 1286 Electrochemical Interface controlled by ZPlot software. The frequency range used was 65 kHz to 0.1 Hz with 10 frequencies per decade and integration time 60 s, with an rms perturbation voltage of 10 mV. Fitting to electrical equivalent circuits was performed with ZView 3.1 software.

All measurements were carried out at laboratory temperature, approx. 25 ± 1 °C. The pH measurements were carried out by digital pH meter micropH 2001 (Crison, UK) with a combined glass electrode.

2.3 Procedures

During the experiments, the blocking of the GCE surface, probably by aminonaphthalene oxidation products, was observed already after the first scan. Because electrochemical pre-treatment of GCE was found not to be efficient, mechanical cleaning of the electrode surface using filter paper and diamond spray (1 μm, Kemet International Ltd., UK) with subsequent rinsing by deionized water was done after each scan. The BDDE was cleaned by electrochemical pre-treatment: between individual measurements, an activation procedure was carried out consisting of stirring and applying a potential of +2.4 V for 15 s to the BDDE in the analyte-containing solution [4]. For CFE no treatment was applied.

Coating of GCE was performed either with 10 μL of 1 % Nafion or 2 × 10 μL of 1 % MWCNT solutions in *N,N*-dimethylformamide (DMF) with a micropipette and allowing the coating to dry at room temperature. The carbon nanotubes were prepared as follows: they were first functionalized [26] in 5 mol L^{-1} HNO_3 in order to introduce active groups at the end and sidewall defects, then 1 mg of functionalized MWCNT were dispersed in 100 μL of DMF and then sonicated during 4 h to ensure a homogeneous mixture [37].

The solutions for voltammetric measurements were prepared by measuring the appropriate volume of stock solution of the substance to be tested and adding BR buffer of the required pH to give a volume of 10 mL. Values of current density (j) used in plots were calculated as I/A, where I is the measured current and A is the geometric area of the electrode. The height of the DPV peak was measured from the straight line connecting the baseline on both sides of the peak. All calibration curves were measured in triplicate and their statistical parameters (e.g., slope, intercept, correlation coefficient, standard deviation) and other mathematical and statistical quantities

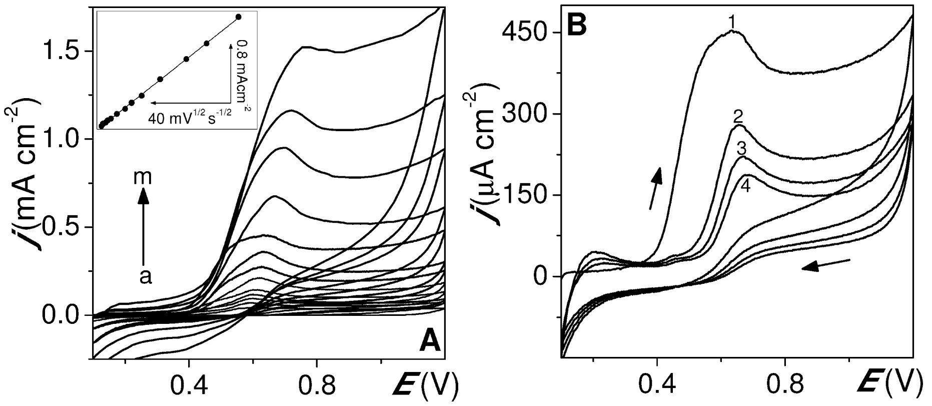

Fig. 1. (A) Cyclic voltammograms of 5×10^{-4} mol L^{-1} 1-AN at GCE in BR buffer pH 4.0 at scan rates 5 (a), 10 (b), 20 (c), 30 (d), 50 (e), 100 (f), 200 (g), 300 (h), 500 (i), 1000 (j), 2000 (k), 3000 (l), and 5000 (m) mV s^{-1}. Inset: Dependence of peak current density of 1-AN on the square root of scan rate. (B) Four consecutive cyclic voltammograms of 5×10^{-4} mol L^{-1} 1-AN at GCE in BR buffer pH 4.0 at scan rate 500 mV s^{-1}.

were calculated (all for the significance level $\alpha=0.05$) [38]. Limits of detection were calculated as $LOD=(3SD)/b$, where SD is standard deviation of intercept and b is slope of the calibration curve.

A sample of river water taken from Mondego river, Parque Verde, Coimbra, Portugal, was used for electroanalysis. The river water was filtered by filter paper, kept in a refrigerator at 4 °C, and analysed within 3 days after sampling. The solutions for analysis were prepared from 9 mL of filtered river water plus 1 mL of BR buffer pH 2.0, total volume 10 mL, and then spiked with 50 μL or 100 μL of the 0.010 M stock solution of analyte (i.e. concentration of analyte in tested solution was 50 or 100 μmol L^{-1}) and directly tested. The concentration in the sample was estimated using the calibration curve.

3 Results and Discussion

3.1 Electrochemical Oxidation of Aminonaphthalenes at GCE

The electrochemical oxidation of 1-AN and 2-AN was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). A study of the scan rate dependence by CV and the pH dependence by DPV was carried out. The mechanism of oxidation was assessed by both techniques.

3.1.1 Cyclic Voltammetry

The electrochemical behavior of 1-AN and 2-AN at GCE was investigated by CV in the potential range from +0.1 to +1.2 V. Cyclic voltammograms obtained at GCE in a 5×10^{-4} mol L^{-1} solution of 1-AN in BR buffer pH 4.0 at different scan rates are depicted in Figure 1A. The linear dependence of current density on square root of scan rate (inset in Figure 1A) indicates that the electrochemical process is diffusion-controlled. A similar behavior was observed for 2-AN (not shown).

A decrease of the oxidation peak currents was observed after successive cycling without cleaning the electrode surface between individual scans, (Figure 1B), a feature common for aromatic amines [7,8]. Their electrooxidation is initiated by the loss of one electron forming a radical cation at the nitrogen atom, which gives rise to dimeric products and polymeric films by rapid follow-up reactions blocking the electrode surface. The electrooxidation of aminonaphthalenes presumably leads to the corresponding radical cations describable by mesomeric forms with the positive charge settled at aromatic rings. These cations undergo further coupling forming simple dimers or polymers. The extension of the positive charge over both aromatic rings is expected to lead to a higher number of coupling modes and therefore, a higher number of anodic voltammetric signals as we described previously for aminonaphthalenes and aminobiphenyls [4,5]. Detailed investigation of the structure of the polymeric films is out of the scope of this study.

3.1.2 Differential Pulse Voltammetry

The effect of pH on the current and peak potential of aminonaphthalenes was measured at GCE in BR buffer with pH values ranging from 2.0 to 11.0. The DP voltammograms of 1-AN are shown in Figure 2A and the dependence of peak potential of 1-AN and 2-AN ($c=5\times10^{-4}$ mol L^{-1}) on pH is shown in Figure 2B. Both, 1-AN and 2-AN, exhibit one peak at pH 2.0 and two peaks in the range of pH 3.0–11.0. With decreasing pH, a gradual shift of the oxidation peak toward more positive potentials was observed, which can be explained by protonation of the nitrogen atom causing a decrease in electron density, resulting in more difficult oxidation. The slopes for peak potential versus pH in the pH range 2.0–4.0 were 50 mV for 1-AN and 49 mV for 2-AN per pH unit, which is close to the theoretical value of 59 mV for an equivalent number of protons and electrons involved in the oxidation prior to the rate determining step. We

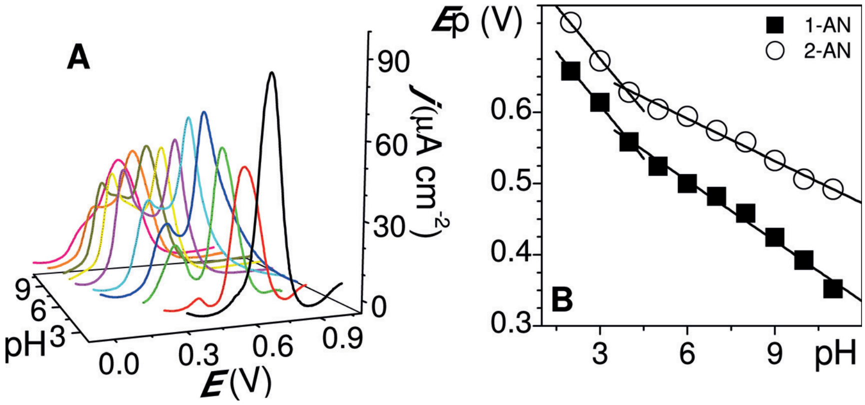

Fig. 2. (A) DP voltammograms of 1-AN measured at GCE in BR buffer pH 2.0–11.0 and (B) pH dependence of peak potential of 1-AN and 2-AN ($c=5\times10^{-4}$ mol L^{-1} of each).

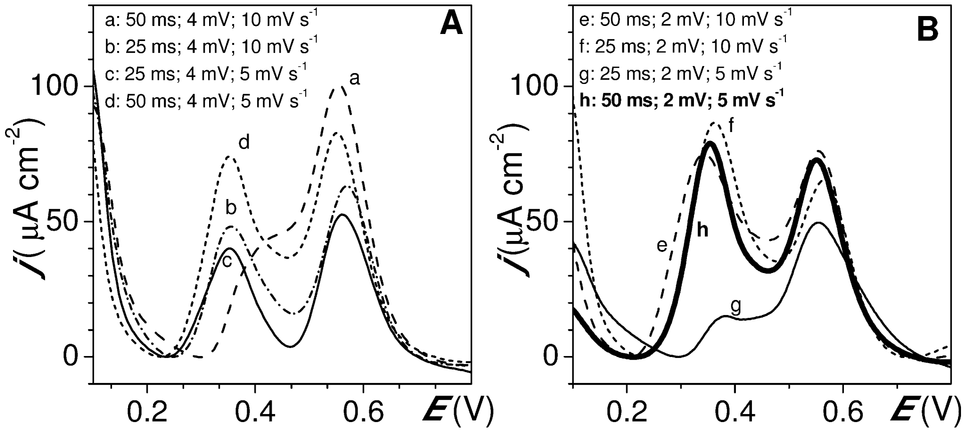

Fig. 3. DP voltammograms of 5×10^{-4} mol L^{-1} 1-AN at GCE in BR buffer pH 4.0 with different DP parameters: constant pulse amplitude 50 mV, constant potential step 4 mV (A) and constant potential step 2 mV (B); the optimum values depicted in bold.

assume that this oxidation step corresponds to the one electron oxidation with loss of one proton of the protonated amino group to give the corresponding aminocation radical Ar-NH$^{2+\bullet}$ [5,7,39,40].

The change in the slope at pH 4.0 is evidently connected to the pK_a values of 1-AN (pK_a=3.92) and 2-AN (pK_a=4.16). At pH values higher than 4.0, the slopes change to 28 mV for 1-AN and 20 mV for 2-AN per pH unit, thus suggesting the loss of two protons per one electron. Presumably, the initial product of the oxidation of nonprotonated aminonaphthalene is Ar–N$^{+\bullet}$ stabilized by its mesomeric forms extending the radical cation over both aromatic rings. For both tested aminonaphthalenes, substantially higher peak currents and symmetric peak shape was observed at pH 2.0; thus BR buffer pH 2.0 was used for further electroanalytical determinations.

The influence of DPV scan parameters on the response of 1-AN at GCE was also investigated. The experiments were carried out for 1-AN ($c=5\cdot10^{-4}$ mol L^{-1}) in BR buffer pH 4.0, where 1-AN gives two peaks, in order to see how the change of parameters influences the shape and the height of both peaks. The parameters were: pulse amplitude (50 mV), pulse time (25 and 50 ms), potential step (2 and 4 mV) and scan rate (5 and 10 mV s^{-1}). As an example, DP voltammograms for potential steps of 4 mV and 2 mV are shown in Figure 3. The optimum values of pulse amplitude 50 mV, pulse time 50 ms, potential step 2 mV and scan rate 5 mV s^{-1} were chosen on the basis of the highest and best shaped peak.

3.2 Voltammetric Determination of Aminonaphthalenes at Bare Carbon-Based and Modified Surfaces

Under the optimised conditions, the determination of aminonaphthalenes was performed by DPV at bare carbon surfaces–GCE, BDDE and CFE. Further, the effect of the modification of the GCE surface with Nafion or multiwalled carbon nanotubes for 1-AN measurement was tested and analytical parameters were compared.

3.2.1 Determination at Bare and Modified GCE

Calibration curves for 1-AN and 2-AN measured under the optimized conditions in the concentration range from 2 to 100 μmol L^{-1} using a GCE as working electrode

Table 1. Analytical parameters from linear dependences for the determination of 1-AN and 2-AN by DPV at different types of electrodes in BR buffer pH 2.0.

Electrode	Linear dynamic range (μmol L^{-1})	Sensitivity (nA μmol^{-1} L cm^{-2})	Correlation coefficient	*LOD* (μmol L^{-1})	Pretreatment	*RSD* [a] (%)
1-AN						
BDD	2–20	282	0.9981	1.4	electrochemical	3.8
CFE	2–20	80	0.9914	3.1	without	16.0
GCE	2–100	257	0.9998	1.6	mechanical	4.3
Nafion/GCE	0.2–20	302	0.9998	0.4	without	9.8
MWCNT/GCE	10–100	229	0.9947	11.6	without	12.9
2-AN						
GCE	2–100	358	0.9998	2.0	mechanical	4.4

[a] repeatability of peak height expressed by relative standard deviation, $c = 20$ μmol L^{-1} , $n = 4$.

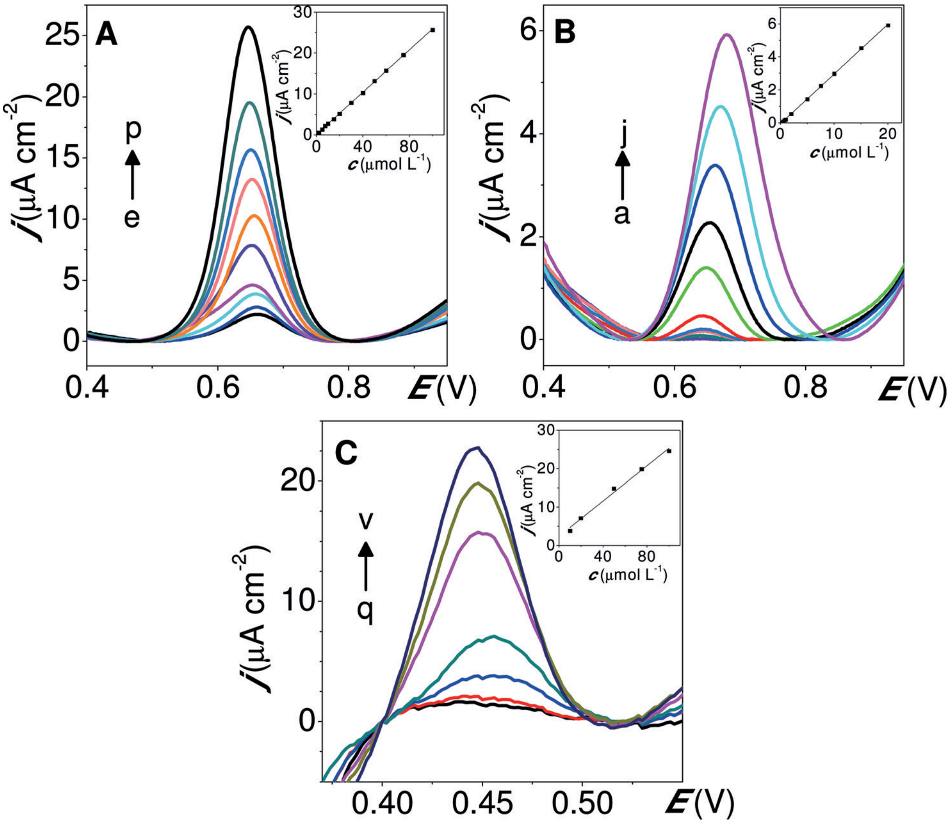

Fig. 4. DP voltammograms of 1-AN at bare GCE (A), Nafion/GCE (B), and MWCNT/GCE (C) in BR buffer pH 2.0; concentration of 1-AN: (A, B) 0.2 (a), 0.5 (b), 0.75 (c), 1.0 (d), 2.0 (e), 5.0 (f), 7.5 (g), 10.0 (h), 15.0 (i), 20.0 (j), 30.0 (k), 40.0 (l), 50.0 (m), 60.0 (n), 75.0 (o), 100.0 (p); (C) 2.0 (q), 5.0 (r), 10.0 (s), 20.0 (t), 50.0 (u), 75.0 (u), 100.0 (v) μmol L^{-1}, subtracted baselines. Insets: Linear dependences of 1-AN concentration on peak current density.

showed a linear dependence over the whole concentration range. The calibration parameters are presented in Table 1 and the linear dependence for 1-AN measured at bare GCE is depicted in Figure 4A. Micromolar limits of detection were obtained, specifically 1.6 μmol L^{-1} for 1-AN and 2.0 μmol L^{-1} for 2-AN.

In order to increase the response towards 1-AN, two different strategies were then investigated: modification of the glassy carbon surface with Nafion permselective membrane or with multiwalled carbon nanotubes. Selected analytical parameters from calibration dependences are shown in Table 1 and a comparison of DP voltammograms of all investigated bare and modified surfaces is depicted in Figure 5. In the case of Nafion modified GCE (Nafion/GCE), the calibration dependence is linear in the range from 0.2 to 20 μmol L^{-1} (Figure 4B). For GCE modified by MWCNT (MWCNT/GCE), the calibration dependence is linear in the range from 10 to 100 μmol L^{-1} (Figure 4C) and the considerable shift of peak potential to a less positive value $E_p = +450$ mV is evident

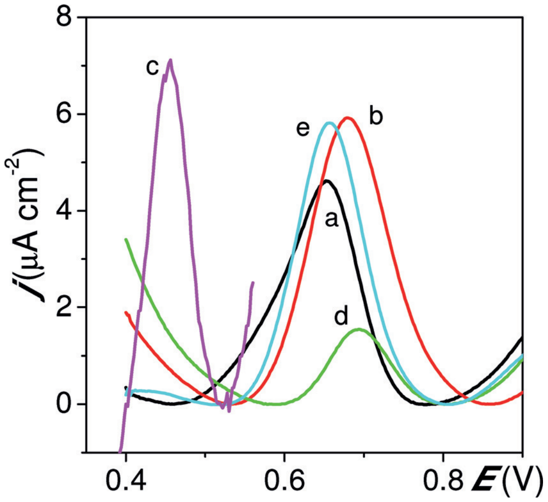

Fig. 5. DP voltammograms, after baseline subtraction, of 20 µmol L^{-1} 1-AN at bare GCE (a), Nafion/GCE (b), MWCNT/GCE (c), CFE (d), and BDDE (e) in BR buffer pH 2.0.

(Figure 5) attributable to the electrocatalytic properties of MWCNT. The sensitivity at MWCNT/GCE decreased (229 nA µM^{-1} cm^{-2}) and at Nafion/GCE increased (302 nA µM^{-1} cm^{-2}) compared to bare GCE (257 nA µM^{-1} cm^{-2}). Also, regarding the other characteristics, Nafion/GCE performed better than either bare GCE or MWCNT/GCE, i.e. linear dynamic range over two orders of magnitude of concentration, low noise and submicromolar *LOD* of 0.4 µmol L^{-1}. Another advantage of both modified surfaces is no necessity to clean the electrode surface between measurements.

3.2.2 Determination at Different Electrode Surfaces

Beside GCE, 1-AN was investigated at other carbon-based bare surfaces, namely carbon film electrodes obtained from electrical resistors and boron doped diamond film electrodes. DP voltammograms in 20 µmol L^{-1} 1-AN for all investigated surfaces are depicted in Figure 5 and a comparison of analytical figures of merit is given in Table 1. 1-AN exhibited one peak at a similar potential for BDDE (+655 mV) and GCE (+657 mV), and was slightly more positive for CFE (+690 mV). The calibration dependences at BDDE and CFE were linear in a shorter range than at GCE (2–20 µmol L^{-1} compared with 2–100 µmol L^{-1}). The detection limits for BDDE and GCE are comparable (ca. 1.5 µmol L^{-1}), the higher *LOD* for CFE (3.1 µmol L^{-1}) being explained by the lower sensitivity of this electrode material.

Blocking of the electrode surface was a problem for all types of bare electrode surface. However, this could be overcome by mechanical polishing at GCE or by anodic pre-treatment of BDDE. Thus, bare electrodes, after mechanical or electrochemical cleaning, exhibit better peak height repeatability than modified electrodes which do not require any cleaning if a slightly higher *RSD* can be accepted.

It can be concluded that Nafion/GCE is the most sensitive electrode material of those tested, with the lowest *LOD*, and with simple handling. However, highly reproducible responses, with easy recovery of the electrode surface can be obtained at unmodified GCE and this electrode exhibited a wider linear range, which is more suitable for practical applications.

3.3 EIS Characterisation of 1-AN and 2-AN

Electrochemical impedance spectroscopy measurements were carried out in BR buffer pH 2.0 and with addition of 50 µmol L^{-1} 1-AN and 2-AN at GCE at different potentials, and comparison with BDDE was also performed for 1-AN. The potentials used were 0.0 V, where no reaction occurs, +0.65 V and +0.74 V, where oxidation of 1-AN and 2-AN, respectively, take place. Complex plane impedance spectra of 1-AN and 2-AN are shown in Figure 6.

The spectra were fitted with the same equivalent circuit, consisting of a cell resistance, R_Ω, in series with a parallel combination of a constant phase element, CPE$_1$ and a resistance, R_1, this last being in series with another parallel combination of a double layer constant phase element, CPE$_{dl}$ and a charge transfer resistance, R_{ct}. The CPE are modelled as non-ideal capacitors, described by $CPE = -(i\omega C)^{-\alpha}$, where ω is the angular frequency and the α exponent reflects a non-uniform surface. The CPE$_1$ and R_1 are associated with the film formed at the electrode surface due to the adsorption of 1-AN or 2-AN. Data from the equivalent circuit fittings are presented in Table 2.

All spectra show similar behaviour with the addition of analyte in the supporting electrolyte, namely at 0.0 V almost no differences in the spectra were obtained, while at +0.65 V and +0.74 V, respectively, the values of the impedance significantly decreased in the presence of 1-AN or 2-AN, meaning that electron transfer occurs at this potentials. The values of cell resistance were 20 Ω cm^2 for GCE$_1$, 30 Ω cm^2 for GCE$_2$ and 60 Ω cm^2 for BDDE. The differences in the values are due to the different types of electrode used, and this is valid for all the other circuit elements. For BDDE, the values of α_{dl} are closer to 1.0 and lower values for CPE$_{dl}$ were obtained compared to GCE, showing that this electrode is more capacitive than GCE. The most significant alteration is observed for the charge transfer resistance, consistent with easier electron transfer in the presence of analyte (1st spectra). The process at GCE was faster than at BDDE, as reflected by the lower R_{ct} values. When recording again the spectra in the presence of analyte after a short period, the value of the charge transfer resistance increases further (2nd spectra), showing that the aminonaphthalenes adsorb on the surface of the electrode, hindering electron transfer, in agreement with cyclic voltammetry.

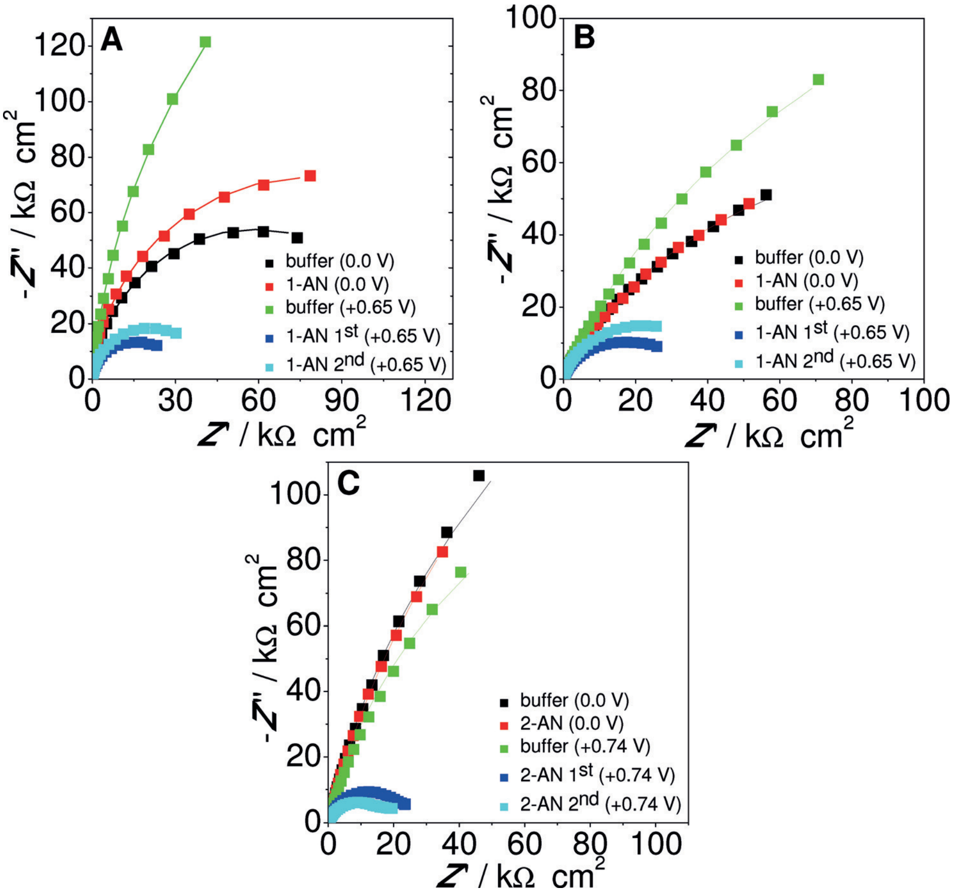

Fig. 6. Complex plane impedance spectra for 1-AN at BDDE (A) and GCE (B) and for 2-AN at GCE (C) in BR buffer pH 2.0 at different potentials. Lines indicate equivalent circuit fitting.

Table 2. Data obtained from equivalent circuit fitting of the impedance spectra at GCE for 1-AN and 2-AN and at BDD for 1-AN in BR buffer at pH 2.0 ($c = 50\ \mu\mathrm{mol\,L^{-1}}$ for 1-AN and 2-AN).

Electrode	Potential (mV)	Analyte	R_1 (kΩ cm²)	CPE$_1$ ($\mu\mathrm{F\,cm^{-2}\,s^{\alpha-1}}$)	α_1	R_{ct} (kΩ cm²)	CPE$_{dl}$ ($\mu\mathrm{F\,cm^{-2}\,s^{\alpha-1}}$)	α_{dl}
GCE$_2$	0	buffer	12.5	5.81	0.89	209	10.6	0.56
		1-AN	11.5	6.09	0.89	185	11.5	0.60
	650	buffer	11.8	4.82	0.91	332	7.04	0.64
		1-AN 1st	10.3	4.53	0.91	24.9	13.1	0.65
		1-AN 2nd	12.5	3.53	0.92	33.5	8.89	0.64
BDD	0	buffer	0.143	5.95	0.96	111	3.78	0.97
		1-AN	0.092	6.32	0.95	149	3.43	0.99
	650	buffer	0.195	8.53	0.93	522	2.55	1.0
		1-AN 1st	0.151	8.69	0.92	31.1	2.92	1.0
		1-AN 2nd	0.130	7.08	0.94	40.9	4.12	0.98
GCE$_1$	0	buffer	0.051	6.77	0.72	971	5.88	0.93
		2-AN	0.050	5.21	0.71	849	11.3	0.88
	740	buffer	0.053	7.65	0.70	508	5.86	0.93
		2-AN 1st	0.066	15.1	0.59	20.9	5.47	0.93
		2-AN 2nd	0.062	9.36	0.63	27.3	6.18	0.90

3.4 Simultaneous Determination of 1-AN and 2-AN and Recovery in Water Samples

On the basis of the presence of one peak and the difference of peak potentials of 1-AN ($E_p = +658$ mV) and 2-AN ($E_p = +726$ mV) at GCE, DPV was used for the simultaneous determination of the two analytes in a mixture in BR buffer pH 2.0 as supporting electrolyte. Each aminonaphthalene was measured by increasing its concentration in the range from 2 to 10 $\mu\mathrm{mol\,L^{-1}}$, while keeping the concentration of the other aminonaphthalene at a constant value of 10 $\mu\mathrm{mol\,L^{-1}}$. The corresponding DPV are

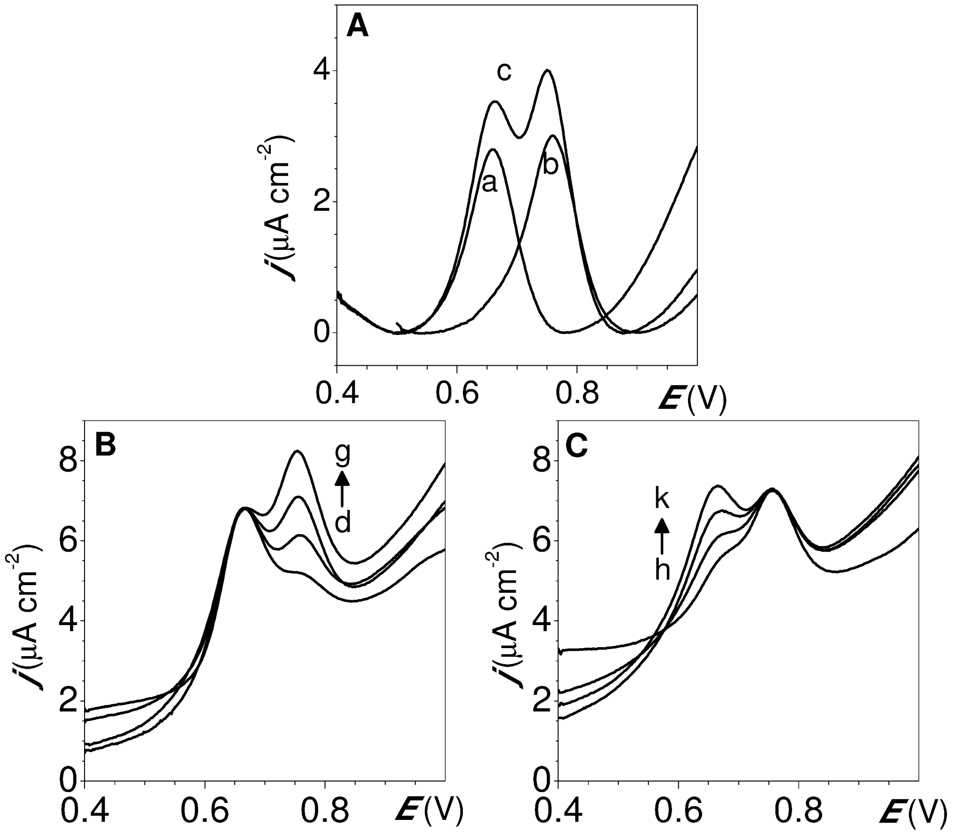

Fig. 7. (A) DP voltammograms of 1-AN (a), 2-AN (b) and mixture of 1-AN and 2-AN (c) ($c=10$ μmol L^{-1} of each) at GCE in BR buffer pH 2.0; (B) and (C) DP voltammograms of mixture of 1-AN and 2-AN; (B) constant concentration of 1-AN (10 μmol L^{-1}) and different concentrations of 2-AN: 2 (d), 5 (e), 7.5 (f), and 10 (g) μmol L^{-1}; (C) constant concentration of 2-AN (10 μmol L^{-1}) and different concentrations of 1-AN: 2 (h), 5 (i), 7.5 (j), and 10 (k) μmol L^{-1}.

Table 3. Recovery of 1-AN and 2-AN in model samples of river water, $n=5$, measured at GCE.

Analyte	Concentration added (μmol L^{-1})	Concentration found (μmol L^{-1})	Recovery (%)
1-AN	50	51 ± 1.9	98–106
	100	95 ± 4.1	91–99
2-AN	50	46 ± 2.0	88–96
	100	91 ± 3.7	87–95

shown in Figure 7. The responses showed linear dependences in this range and micromolar limits of detection were obtained, namely 1.9 and 1.6 μmol L^{-1} for 1-AN and 2-AN, respectively.

The practical applicability of the proposed method was tested by the determination of 1-AN and 2-AN in model samples of river water (Table 3). The model samples were prepared as described in section 2.3, testing concentrations of 50 and 100 μmol L^{-1} for each analyte. For 1-AN, recoveries between 91 and 106 % were obtained and for 2-AN, the recoveries ranged from 87 to 96 %, the relative standard deviation for 5 successive measurements, being < 5 %.

4 Conclusions

A comparison of bare carbon-based surfaces, namely glassy carbon, carbon film and boron doped diamond, with a GCE surface modified by Nafion permselective membrane and multiwalled carbon nanotubes for the electroanalysis of 1- and 2-aminonaphthalene was performed. Blocking of the electrode surface by reaction by-products occurred on all types of electrode surfaces. For 1-AN, similar detection limits were achieved for bare surfaces: at BDDE 1.4 μmol L^{-1}, at GCE 1.6 μmol L^{-1} and at CFE 3.1 μmol L^{-1}, for the last electrode the sensitivity was markedly less than with the other electrode materials. Even though it was expected that there would be an increase in sensitivity as reported in many studies for MWCNT/GCE [23–25], no such effect was observed for the compounds studied here. Nafion/GCE offers the lowest limit of detection of 1-AN (0.4 μmol L^{-1}), and thus is useful only for lower concentrations range (0.2–20 μmol L^{-1}).

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